

Studies on the Role of Organophosphites in Polyester Blends: I. ^{31}P Nuclear Magnetic Resonance Spectroscopy

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Synopsis

The utility of ^{31}P magic angle spinning (MAS) nuclear magnetic resonance (NMR) for the identification of organophosphite polymer additives, their hydrolysis products, and for the determination of their concentration is demonstrated for bis-(2,4-di-*t*-butylphenyl) pentaerythritol diphosphite (BTBP) in polycarbonate. This additive undergoes a complex process of hydrolysis that leads to the formation of at least three new phosphorus species. High-resolution solution ^{31}P NMR is used to help in the identification of the products of the stabilizer chemistry.

INTRODUCTION

Polyester blends are known to undergo ester exchange reactions and random reesterification during melt compounding and processing. Since the properties of a blended, multicomponent system depend on the extent of transesterification, these properties will change with processing time. This alteration in properties has been demonstrated in various studies of blends before and after transesterification.¹⁻³ Among the various stabilizers used to stop or, at least, control transesterification phosphite compounds are known to be effective in polyester blends.⁴ The exact mechanism for the stabilizing effect of the phosphites is unknown. One suggestion is that the phosphites can complex, or otherwise neutralize, residual trace metal species that catalyze the transesterification reaction, as suggested by the studies of Devaux et al.⁴

An effective stabilizer for polyethylene terephthalate (PET) is bis(2,4-di-*t*-butyl phenyl pentaerythritol) diphosphite (BTBP), sold as Ultrinox 624 by Borg Warner Chemicals. Usually, a fraction of a percent of stabilizer is sufficient to render the polymer stable.⁵ This stabilizer is also effective in blends of PET with polycarbonate (PC) and polyarylate (PAR).⁵ A convenient method for incorporating the stabilizer is to first prepare a concentrate of the stabilizer in the polymer, an approach similar to the color concentrate technique. Subsequent blending takes the concentration of the stabilizer to the desired final level. The number of processing steps, however, increases the likelihood of partial loss of the stabilizer or its effectiveness via undesirable chemistry. Hence, it is important to be able to track two parameters: (1) the concentration of the phosphite stabilizer in the concentrate and final blend and (2) the extent of phosphite conversion to other moieties during the successive steps in processing. Likewise,

it is important to have a technique to assist in understanding the chemistry of BTBP, or any phosphite stabilizer, for the control of transesterification.

This report describes an analytical technique for the determination of phosphite concentration and for tracking the chemistry of phosphites in polymer concentrates and final blends by ^{31}P magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy.⁶ Phosphorus-31 MAS NMR is useful because it can determine, through the chemical shift interaction, the identity of phosphorus species present in the solid state and, to high precision, the relative and absolute concentration of these moieties. Phosphorus is a relatively sensitive nucleus to NMR (about $\frac{1}{3}$ th that of hydrogen), and the technique can be used to detect the presence and identify phosphorus species down to the 0.2 wt % level. Additionally, high-resolution solution state ^{31}P NMR is applied in this study to verify the identity of chemical species that result from the degradation reactions of BTBP. In the second paper of this series,⁷ the implications of the chemistry observed for the BPBT are discussed in relationship to the thermal stability of blends.

EXPERIMENTAL

Concentrate Preparation. Low molecular weight PC (Calibre 300-15) and high molecular weight PC (Calibre 300-3) were received from Dow Chemical Company. Ultrinox 624, bis(2,4-di-*t*-butyl phenyl pentaerythritol) diphosphite (BTBP), an organophosphite stabilizer, was supplied by Borg-Warner Chemicals. Three concentrates of Ultrinox 624 (10% nominal value) in polycarbonate were prepared in a twin-screw extruder. The principal differences are listed in Table I. All of the concentrates were prepared by first wetting the PC with 0.2 wt % of epoxidized soy bean oil. The wetted PC was then mixed with BTBP (10 wt %) and mechanically tumbled for 30 min. The mixture was then extruded in a twin-screw extruder. The temperature setting at the extruder varied from 230 to 250°C. The extrudate was quenched in water and pelletized. For the MAS experiment, pellets were cryogenically ground. Powders were allowed to return to ambient temperature in the grinding tube to minimize moisture condensation.

Blend Preparation. PAR, PC, and PET were blended in a Haake mini extruder model 245 with temperature settings of 280/300/290°C. The die section was set at 280°C. BTBP was estimated at 0.5 wt % in the final blend.

TABLE I
Summary of Concentrate Preparation in Twin Screw

BTBP ^a concentrate	Polycarbonate (Dow's caliber)	Drying conditions	Compounding atmosphere
A	300-15	Mild	Air
B	300-15	Rigorous	N ₂ blanket
C	300-3	Rigorous	N ₂ blanket

^a Ultrinox 624 (Borg Warner Chemicals); nominal 10 wt %.

Further information on blend preparation may be found in the second paper of this series.⁷

BTBP Solutions. The degradation chemistry of Ultrinox 624 and Ultrinox 626 (identical phosphite with an amine stabilizer) was checked by heating the powders at 270°C for 30 min and then at 100°C for 16 h in a furnace under ambient air. One sample of Ultrinox 624 was heated in the presence of a small amount of added H₂O. The heated materials and samples of untreated Ultrinox 624 and 626 were dissolved in deuterated chloroform. The treated samples were partially insoluble in CDCl₃. The undissolved material was filtered out before the ³¹P NMR spectrum was acquired and was not further analyzed.

Phosphorus-31 MAS NMR. Phosphorus-31 MAS NMR spectra were acquired using a Bruker MSL 300 spectrometer (³¹P resonance at 121.5 MHz) and a Bruker MAS probe. Typical spinning speeds were 3–4 kHz. The internal volume of the rotor was approximately 750 mm³. Sample weight was 400 mg. Acquisition of the MAS-averaged free induction decay was in the presence of high-power proton decoupling (in excess of 80 kHz) following a 1.5 ms ¹H–³¹P cross polarization contact sequence to enhance the ³¹P signal.⁸ Following standard practice, this experiment is referred to as CPMAS. The recycle time was held to 10 s to ensure complete thermal relaxation of the protons. The CPMAS signals were processed using standard Fourier transformation and phasing.⁹ Chemical shifts are referenced to external 85% phosphoric acid with negative shifts representing upfield resonances. In addition to CPMAS, the total suppression of spinning sidebands (TOSS) experiment was also employed.¹⁰ This sequence removes sidebands from the spectrum and is useful when sidebands are potentially overlapping significant spectral features. However, TOSS can lead to erroneous conclusions when quantitative data is desired, and so this sequence was not employed throughout. For some spectra, a TOSS protonated phosphorus suppression (TOSS PPS) experiment was employed.¹¹ For this experiment, a delay time with the decoupler switched off is inserted prior to acquisition. The effect of this delay is to remove, or partially reduce, resonances from phosphorus atoms located close to or directly bonded to hydrogen.¹⁰ TOSS was also employed following use of a single 90° pulse for the creation of transverse magnetization. This experiment, referred to as TOSS FID, is sensitive to phosphorus atoms in mobile sites.⁶ The recycle time for TOSS FID was 1 s.

Phosphorus-31 Solution NMR. Broad-band proton-decoupled solution state ³¹P NMR spectra were also acquired on the Bruker MSL 300 using a Bruker 10-mm solution probe. Effects of the nuclear overhauser enhancement, which cause anomalous signal intensities, were neglected. The FIDs were signal averaged until the noise level in the Fourier transform was acceptable. Following acquisition, standard Fourier transformation and spectral phasing were applied. The spectra were referenced by spiking some samples with triphenylphosphate, resonating at –18.70 ppm with respect to 85% phosphoric acid, with downfield resonances at more positive values of ppm.

RESULTS AND DISCUSSION

Solid State ³¹P NMR of BTBP. Phosphorus-31 CPMAS spectra of neat BTBP (Ultrinox 624) spun at two different rotor speeds are illustrated in

Figures 1a and 1b. The unambiguous differentiation of the isotropic chemical shift line for the BTBP (indicated by the arrow at 115.5 ppm) from the sidebands is possible since the isotropic line position remains unchanged with rotor speed. The positions of the sideband, on the other hand, move with changes in the rotor speed. In general, the isotropic chemical shift line does not have to be more intense than the sidebands, as is sometime presumed. This assignment may be verified by the use of sideband suppression pulse sequences. TOSS techniques, however, are less quantitative than the CPMAS sequence. An isotropic shift line from an impurity (broad peak centered at ca. 7 ppm) is tentatively identified as an amorphous orthophosphate or phosphonate on the basis of the chemical shift alone. These two types of phosphorus have isotropic chemical shifts in this region of ^{31}P chemical shift range.¹² The identity of the impurity type was clarified using solution state ^{31}P NMR, as described shortly. As determined by integration of the total signal including the 7-ppm feature, the impurity represents 3% of the total phosphorus.

The isotropic chemical shift of the BTBP phosphite, 115.5 ppm, is consistent with shift values for structurally similar phosphites in solution.¹² As with ^{13}C

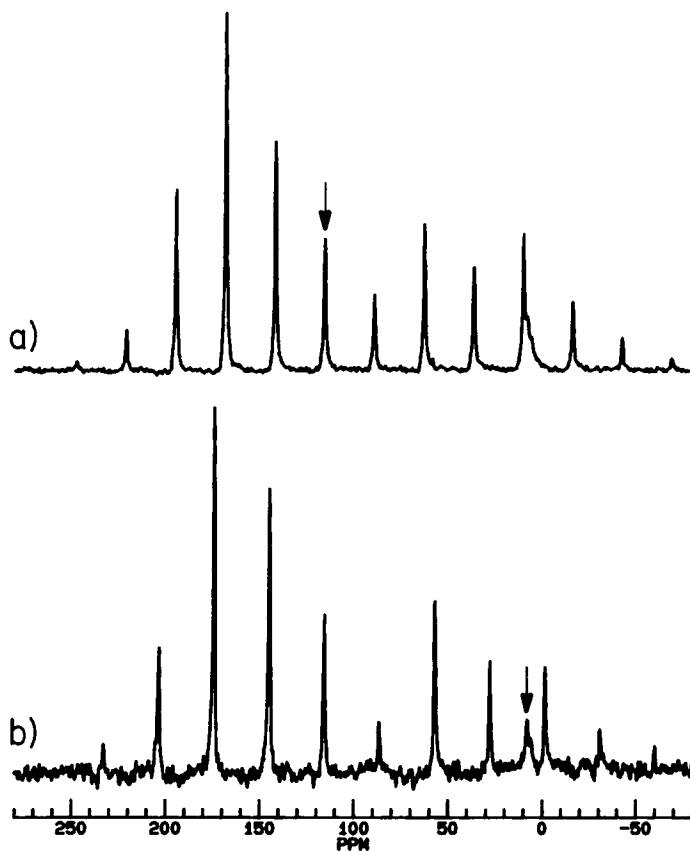


Fig. 1. Phosphorus-31 CPMAS spectra of neat BTBP (26% by weight in a nonphosphorus-containing organic binder): (a) 3200 kHz, 100 acquisitions, arrows indicate isotropic chemical shifts; (b) 3500 kHz, 10 acquisitions. Both spectra represent 256 acquisitions at 120.5 MHz using a 2-ms contact pulse and 10-s recycle time.

and ^{29}Si , ^{31}P solution state chemical shifts and solid state isotropic shifts from MAS for the same compound are generally close if not equivalent.¹³ Organophosphites can undergo oxidation to an organophosphate ester or undergo hydrolysis to an organophosphonate.¹⁴ The isotropic chemical shift of these species should be ± 10 ppm to that of 85% phosphoric acid at 0 ppm.¹²

Solid State ^{31}P NMR of Concentrates. The CPMAS spectrum of concentrate A is shown in Figure 2a. The overall increase in linewidth in the spectra of the PC/BTBP concentrate relative to that of the neat BTBP reflects the loss of crystallinity introduced by the compounding process. A CPMAS

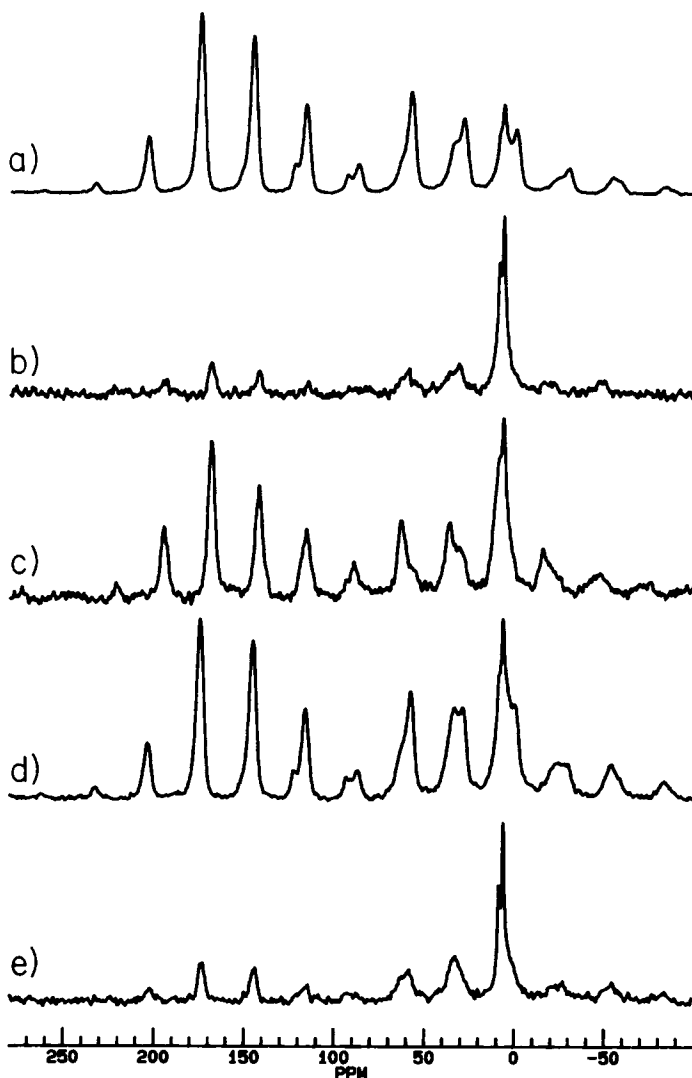


Fig. 2. Phosphorus-31 CPMAS spectra of the PC/BTBP concentrate A: (a) as extruded, 3500 kHz, 14,000 acquisitions; (b) after drying in air-circulating oven, 16 h at 100°C, 3200 kHz; (c) after drying under vacuum without heating, 3200 kHz; (d) clear pellets of concentrate A, 3500 kHz; (e) cloudy pellets of concentrate A, 3500 kHz. All spectra represent 256 acquisitions at 120.5 MHz using a 2-ms contact pulse and 10-s recycle time.

spectrum for the concentrate after 16 h heating in an air-circulating oven at 100°C is illustrated in Figure 2b. The spectrum following vacuum drying is shown in Figure 2c. There is a significant increase in the intensity of the resonances near 7 ppm for samples heated under ambient conditions. Following heating in air, a fraction of the pellets turned from clear to cloudy white. The spectra of the clear and cloudy pellets are illustrated in Figures 2d (clear) and 2e (cloudy). An increase in the band intensity of the resonance at 7 ppm, relative to that of the unheated sample, is apparent in the spectrum of both samples. This impurity material is predominant in the spectra of the cloudy pellets (Fig. 2e). In addition, the cloudy pellets' spectrum contains three resonances from impurities, two represented by sharp peaks at 5.9 and 8.3 ppm and one by a broad peak at 7 ppm, identical to that originally observed in the neat phosphite sample. This broad feature is responsible for the accompanying broad sidebands observable in Figures 2b and 2e.

Without the cross polarization used in CPMAS, the signal from phosphorus in the BTBP does not appear in the TOSS FID spectrum. This can be seen in the comparison of Figure 3a, CPMAS, with 3b, TOSS FID. This indicates that the phosphorus moiety in the BTBP, as present in concentrate A, is in a relatively immobile environment. On the other hand, the resonances around 7 ppm must be from a phosphorus species in mobile or easily relaxed environments, since they are detected in the TOSS FID experiment. The mobility of the phosphorus sites eliminates the possibility of using TOSS PPS to determine the issue of phosphorus protonation,¹¹ since in this sample, high mobility prevents suppression of the protonated phosphorus resonances even though these resonances will be shown to be protonated in the polymer blends. As is well known, the time constant for suppression of a resonance under TOSS PPS conditions is a complex function of not only neighboring proton density but also local mobility.¹⁵ The TOSS FID spectrum, Figure 3b, confirms that three resonances appear near 7 ppm: two sharp peaks sitting on a broader feature. The broader feature is responsible for the sidebands centered around 7 ppm observed in the CPMAS spectra of this concentrate, as seen in Figure 2e.

The cloudiness observed in some of the pellets of concentrate A after heating in an air circulating oven may be related to the increase in the species resonating near 7 ppm. Degradation of the BTBP is also observed if the unheated pulverized pellets of that concentrate are exposed to ambient air for about 30 days, as is illustrated in Figure 3c. The chemistry occurring in the aged concentrate appears to be similar to that of samples heated in air. Thus, the new species are either oxidation or hydrolysis products of BTBP, as little chemistry transpired in the vacuum environment. A background spectrum is given in Figure 3d, the ³¹P MAS NMR spectrum of original polycarbonate. No phosphorus species are in the polycarbonate and no experimental artifact is responsible for the additional isotropic resonances that are being observed. The resonances other than the BTBP result from reactions involving the BTBP.

The concentration of BTBP in the PC/BTBP concentrate was determined by integrating over the total spectrum for comparison against the integral of spectra of weighed mixtures of BTBP powder and of powdered PC. This procedure was carried out for five sample batches of concentrate dried either in air or in vacuum. The concentrations determined in this fashion for the phosphite prior to any reactions ranged between 5 and 15%. This range of variability

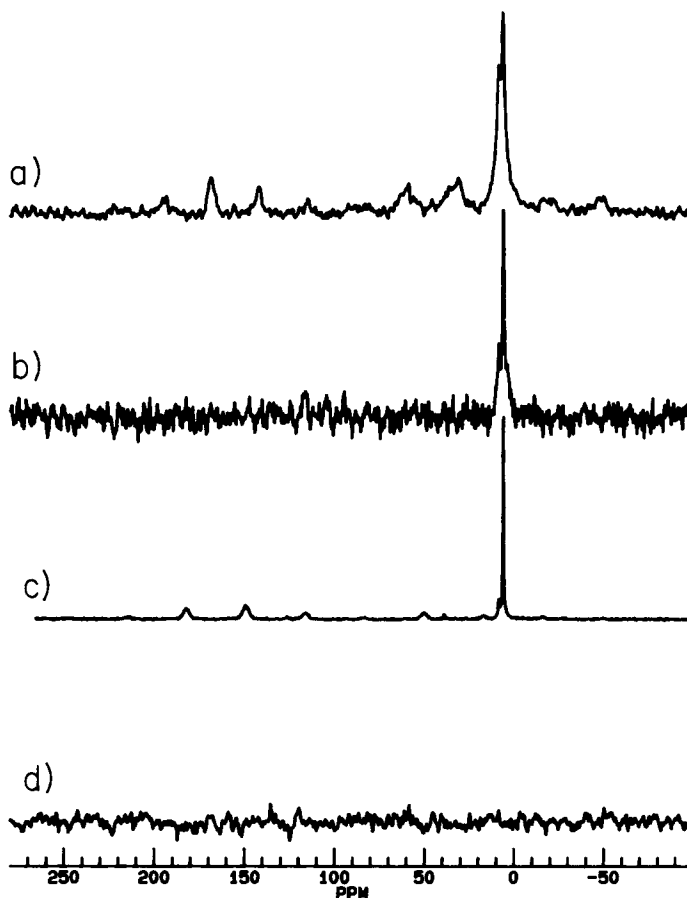


Fig. 3. Phosphorus-31 NMR spectra of the PC/BTBP concentrate A: (a) CPMAS spectrum of concentrate A dried in an air-circulating oven at 100°C (same as Fig. 2b); (b) TOSS FID of the concentrate dried in oven at 100°C; (c) CPMAS spectrum of pulverized concentrate A stored in ambient conditions for 30 days; (d) CPMAS spectrum of neat polycarbonate (Dow's Calibre 300-15).

for individual MAS samples (400 mg) around the nominal concentration of 10 wt % BTBP implies that more than one sample should be measured if this, or for that matter any technique, is to be quantitative.

Solid State ^{31}P NMR of Polymer Blends. The CPMAS NMR spectrum of the actual PC/BTBP concentrate (concentrate A) used to produce the polymer blend is shown in Figure 4a. This material was dried for 16 h in an air circulation oven at 110°C. As this spectrum was acquired to a high signal-to-noise (S/N) ratio, it is possible to see a weak impurity line at 95 ppm. The isotropic peaks are indicated by arrows: BTBP at 115.5 ppm, impurities at 95 and approximately 7 ppm. Phosphorus-31 MAS NMR spectra of the ternary blend produced using the PC/BTBP concentrate are shown in Figures 4b–4d. The ^{31}P MAS NMR spectrum of the stabilizer is altered after compounding, as illustrated in Figure 4b. The signal-to-noise ratio in this spectrum is consistent with a concentration of phosphorus species at ca. 0.5 wt %. The positions

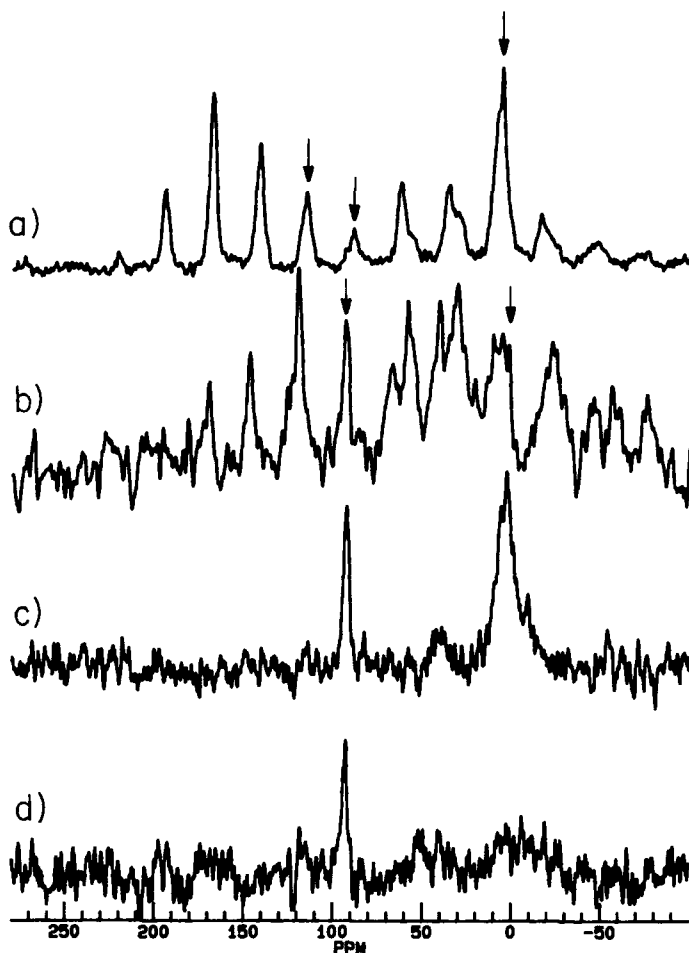


Fig. 4. Phosphorus-31 spectra of blends prepared from PC/BTBP concentrate A, 3200 kHz: (a) CPMAS spectrum of the PC/BTBP concentrate after drying under vacuum for 16 h in an air-circulating oven; (b) CPMAS spectrum of a polymer blend prepared using the PC/BTBP concentrate; (c) TOSS spectrum of the same blend, 36,000 acquisitions, 2-s recycle delay; (d) TOSS PCS spectrum using a 40- μ s delay of the same blend, 12,000 acquisitions.

of the isotropic peaks are again indicated by arrows. As is apparent, the BTBP resonance peak at 115.5 ppm is gone.

To verify the absence of the BTBP, the spectrum of the blend was also acquired using TOSS and TOSS PPS sequences.¹⁰ In this way, the overlapping and complicating sidebands are eliminated, and only the isotropic resonances are visible in the spectra. The TOSS spectrum, illustrated in Figure 4c, shows only the resonances at 95 and ca. 7 ppm. There appears to be a broad peak at ca. 42 ppm. This may be an additional product of the chemistry of BTBP. The identification of this peak will not be attempted. The TOSS PPS spectrum for a delay time of 40 μ s is illustrated in Figure 4d. The line at 95 ppm is only slightly reduced in intensity, but the 7-ppm resonance is absent. As already indicated, the suppression of a resonance under TOSS PPS conditions is a

complex function of local mobility and neighboring proton density.¹⁵ In a study of the intensity loss as a function of delay in signal acquisition for BTBP and diphenyl phosphate, reductions of about 30% are seen for delays up to 120 μ s.¹¹ Thus, the elimination of the resonance at 7 ppm in 40 μ s indicates a marked difference in the phosphorus type. This species is most likely a protonated phosphorus species in a relatively rigid environment. This differs from the case of the concentrates where molecular mobility is quite high as evidenced by the results from the TOSS FID experiment. Thus, the 7-ppm species in the blend cannot be a phosphate, the product of oxidation of the phosphite. An appropriate alternative is a phosphonate resulting from hydrolysis of the phosphite triester. For such a species, which has a proton directly bonded to the phosphorus, one expects short TOSS PPS delays to produce complete loss of intensity.

As was pointed out in the discussion of Figure 4, for the ternary blend prepared with concentrate A, the processing required in blending advances the reactions observed in making the concentrate. By contrast, in the ternary blend prepared with concentrate C, which uses the high molecular weight PC under rigorous drying conditions (see Table I), there is no indication of the 7-ppm resonance. The CPMA spectra of these materials are illustrated for the concentrate (Fig. 5a) and for the corresponding blend (Fig. 5b). The resonance at 95 ppm is observed, indicating that this species is not likely a degradation product, but rather a compound in some batches of the Ultrinox 624. This compound may be another phosphite triester, a conclusion that is consistent with the TOSS PPS results discussed previously. This species does not contain a protonated phosphorus. To see whether the drying conditions or difference in molecular weight is responsible for this change in chemistry, a further batch was prepared under rigorous drying conditions using, this time, the low molecular weight PC. This batch is termed concentrate B (Table I). The TOSS spectra of both concentrate B (Fig. 5c) and the corresponding blend (Fig. 5d) contain the 7-ppm peak. In the blend, Figure 5d, the BTBP peak is virtually absent (a small residual peak is still observed in Fig. 5d). It should be mentioned that for both of the concentrates prepared under rigorous drying conditions, concentrates B and C, the spectra were acquired some 10 days after preparation of the concentrates and blends.

Solution State ³¹P NMR Experiments. The study of the BTBP chemistry via solution state ³¹P NMR was motivated by the results from the application of the TOSS FID experiment to the PC/BTBP concentrate A (mild drying) heated in an air-circulating oven. Open air heating of BTBP results in degradation of the phosphite to species, whose solution state ³¹P NMR resonances are near 7 ppm, as illustrated in the series of spectra collected in Figure 6. The spectra of solutions of Ultrinox 624 and Ultrinox 626, Figure 6a and 6b, respectively, show additional features beyond the resonance at 115.5 ppm attributed to BTBP. Both samples produce spectra with the peak at 95 ppm and features at ca. 125 ppm. The Ultrinox 624 shows resonances near 7 ppm. After 10 min at 270°C, Ultrinox 624 shows significant intensity and complex structure near 7 ppm (Fig. 6c). The spectra of similarly treated Ultrinox 626 shows similar structure, but with less intensity. The two materials show the same chemistry. Ultrinox 626, however, reacts at a slower rate. This is attributed to the presence of the amine stabilizer in Ultrinox 626. After 16 h at 100°C (Fig. 6d), there are a large number of closely related products, thus accounting for

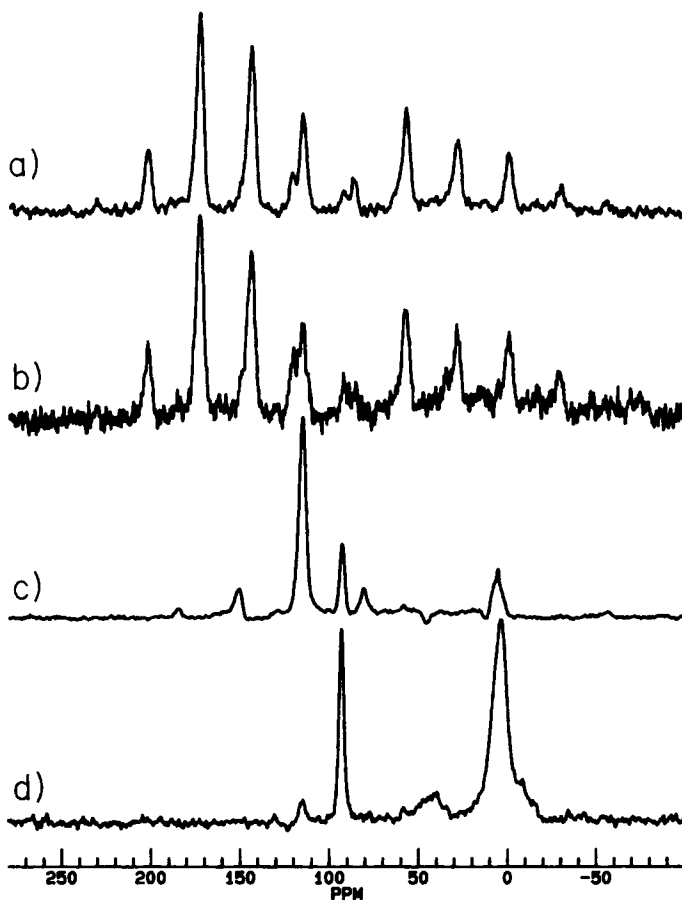


Fig. 5. (a) CPMAS spectrum of PC/BTBP concentrate C; (b) the corresponding polymer blend; (c) TOSS spectrum of concentrate B; (d) the corresponding polymer blend.

the bandwidth of the lowest field peak near 7 ppm. If a few drops of water are added to the Ultrinox 624 powder and heated, the spectrum of the reaction products (Fig. 6e) indicates that all of the original phosphite has disappeared along with the unidentified impurities at 125 and 95 ppm. The proton-coupled spectrum illustrated in Figure 6f shows each of these peaks to be doublets. The coupling constants are all ca. 700 Hz. Coupling constants of this value are consistent with those measured for organic phosphonates, compounds with one P—H bond.¹²

CONCLUSION

The utility of ^{31}P MAS NMR for the determination of the concentration and identities of hydrolysis products of organophosphite additives has been demonstrated on concentrates of polycarbonate and BTBP and blends using these concentrates. The hydrolysis appears to be a complex process that leads to the formation of several phosphonates. The details of the degradation chem-

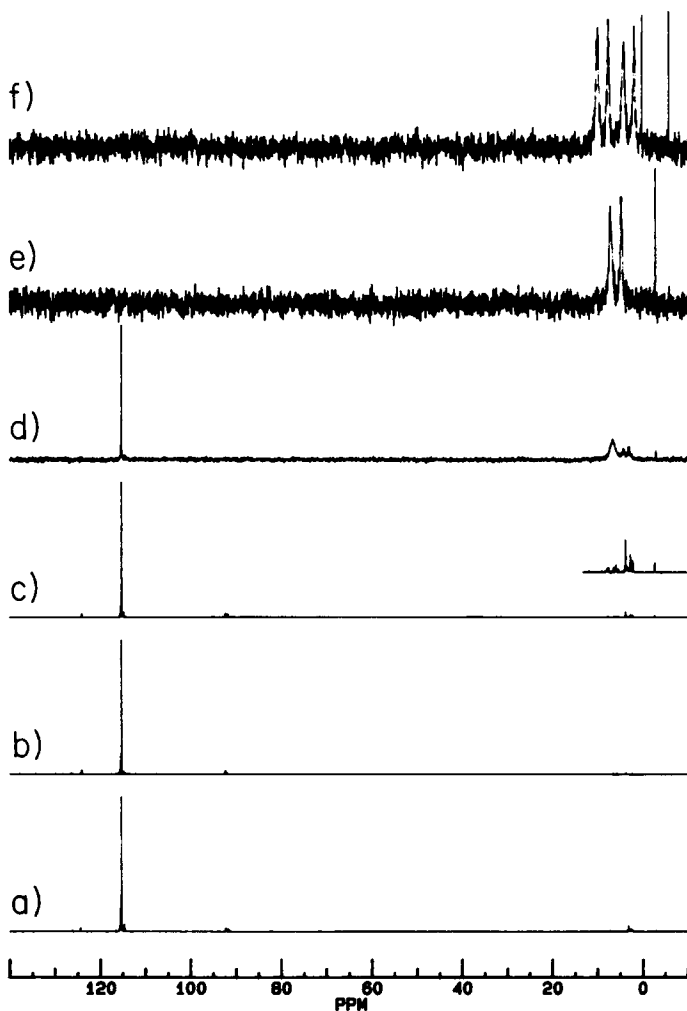


Fig. 6. Solution state ^{31}P NMR spectra of Ultranox 624 (all solutions in CCL_3D): (a) untreated Ultranox 624; (b) untreated Ultranox 626; (c) Ultranox 624 after 10 min at 270°C ; (d) Ultranox 624 after 16 h at 100°C ; (e) Ultranox 624 spiked with a few drops of water after 16 h at 100°C ; (f) same as (e) without broad band decoupling.

istry of BTBP were elaborated using solution state NMR techniques on samples of Ultranox 624 treated under thermal conditions that mimicked those the material experiences during compounding and blending. The comparison between the solution NMR result, i.e., that BTBP degrades into two or three types of phosphonates, and the solid state data, in which the same types of compounds are being formed, is clear. The correspondence between the resonance frequencies observed in the liquid (Fig. 6e) and the mobile species in the PC/BTBP concentrate, TOSS FID spectrum illustrated in Figure 3b, as well as the major species appearing the blend (Fig. 4c) indicates that the same compounds are being formed. For convenience, these three figures have been brought together and represented in Figures 7a–7c. The response of this res-

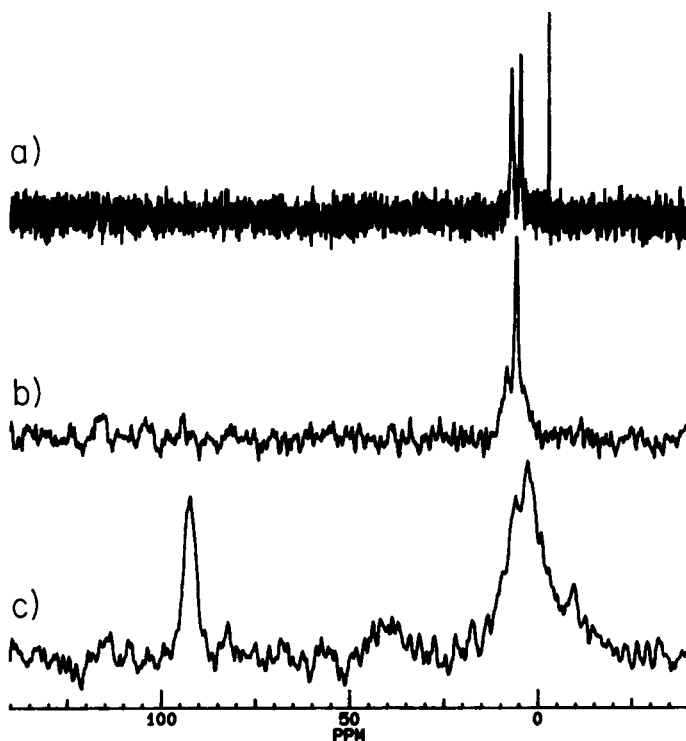


Fig. 7. Comparison of solution and solid state spectra: (a) Ultrinox 624 spiked with a few drops of water after 16 h at 100°C; (b) TOSS FID spectrum of PC/BTBP concentrate A; and (c) TOSS spectrum of the corresponding polymer blend.

onance in the TOSS PPS experiment and the proton-coupled solution experiments indicate that these resonances are associated with a phosphorus-hydrogen bond. Similar chemistry is proceeding and the conclusion concerning the formation of phosphonates is valid for both circumstances.

The analytical technique for quantification of species relies on an external standardization for quantification. This is because integrals over the total phosphorus spectrum from two different rotors containing known masses of sample are compared. The validity of this method requires stability of the gain of the spectrometer, insurance of complete thermal relaxation between pairs of acquisitions, and complete, or at least equivalent, cross polarization for all species present in each sample. Repeated acquisition of the same spectrum under identical conditions confirmed that the receiver gain was constant. Varying the recycle delay as well as the cross polarization times showed, at least for this system, that 1.5 ms represents a maximum in the signal intensity for both phosphorus species before significant relaxation effects occur. These conditions would have to be investigated with each new system. Some 500 acquisitions requiring 1.5 h were acquired for each of the spectra of Figures 2a and 2b, which show signal-to-noise ratios of approximately 6. A 15-h acquisition under the same conditions and on a similar linewidth could detect a 0.3% concentration with a S/N of 1.

The NMR results on the Ultranox solutions, PC/BTBP concentrates, and three component blends all indicate that the stabilizer is being partially hydrolyzed in these systems to phosphonates. The only instance where this chemistry was not observed is in concentrate C (high molecular weight PC; rigorous drying) and the corresponding blend made with it. The phosphonate moieties in concentrates A and B show greater molecular mobility after blending into the three component polymer blend. This can be concluded since the phosphonate resonance appears in the TOSS FID experiment of the PC/BPBT concentrate (Fig. 3b); but when the TOSS PPS experiment is run (results not shown), it is not affected (not suppressed). On the other hand, this same phosphonate, when in the blend, is easily suppressed by the TOSS PPS experiment. Since in both the concentrate and blend, the new species produced are phosphonates, it is concluded that high mobility has effectively averaged the P-H interaction, thus accounting for the negligible signal loss. The reason for this may only be speculated. It may be that the phosphonates are more dispersed in the blend and somehow more tightly caged by the surrounding molecular entities. Another possibility is that the mobility of the phosphonate depends on it being partially dissolved in water, which is removed after blending. Still another possibility is that the phosphonate in the blend is somehow reacted into the polymer chains thus limiting its mobility.

In the second part of this series,⁷ the relationship of the NMR results to the thermal stability of blends and to transesterification will be discussed along with the reactions that lead to the formation of the phosphonate. This second study also takes up the issue of the reduction of mobility of the phosphonate in the blend.

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Received November 8, 1988

Accepted January 6, 1989